Organic light emitting diodes with spin polarized electrodes

Arisi, E.; Bergenti, I.; Dediu, V.; Loi, M. A.; Muccini, M.; Murgia, M.; Ruani, G.; Taliani, C.; Zamboni, R.

Published in:
Journal of Applied Physics

DOI:
10.1063/1.1556118

Publication date:
2003

Organic light emitting diodes with spin polarized electrodes

E. Arisi
Istituto per lo Studio dei Materiali Nanostrutturati ISMN sez. Bologna, Italy

I. Bergenti[a)]
Istituto per lo Studio dei Materiali Nanostrutturati ISMN sez. Bologna, Italy, and Dipartimento di Fisica, Università di Parma and INFM, Parma, Italy

V. Dediu, M. A. Loi, M. Muccini, M. Murgia, G. Ruani, C. Taliani, and R. Zamboni
Istituto per lo Studio dei Materiali Nanostrutturati ISMN sez. Bologna, Italy

(Presented on 14 November 2002)

Electrical and optical properties of Alq_3 based organic light emitting diodes with normal and spin polarized electrodes are presented. Epitaxial semitransparent highly spin polarized $La_{0.7}Sr_{0.3}MnO_3$ were used as hole injector, substituting the traditional indium tin oxide electrode. A comparison of electroluminescence and *IV* curves between similar devices with and without spin polarized injection is reported. The results are a first step in realizing an operating device where the light intensity of the emission can be tuned by controlling the spin injection. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1556118]

I. INTRODUCTION

The efficiency of the organic light emitting diodes (OLEDs) has been continuously improved in the last few years. The interest in OLEDs is mainly driven by potential applications in display industry. However, a deep understanding of charge injection and recombination process in organic materials is lacking. A great effort has been made to enhance the device luminescence working on metal-organic interfaces, morphology, and charge transport in organic material.[1]

Radiative recombination in OLEDs based on undoped π-conjugated molecules arises from singlet excitons annihilation (triplet excitons normally do not contribute to photon emission).[2] The manipulation of the spin of carriers allows one to tune the electroluminescence (EL) efficiency by changing the relative population of singlet/triplet excitons. Recent experiments[3] confirm the possibility of injecting and controlling the transport of spin polarized carriers in π-conjugated organic semiconductors.

Typical OLED electrodes consist of low work function metal as cathode and high work function indium tin oxide (ITO) as a transparent anode. Upon the application of a forward bias, electrons and holes are injected from the electrodes and form excitons inside the organic layer. A spin polarized OLED has electrodes made by spin polarized metallic ferromagnetic thin films; varying their mutual magnetization with an external magnetic field, the singlet/triplet rate should be modified. In this article, we present preliminary results of the substitution of standard OLED electrodes with spin polarized ones.

II. MATERIALS AND METHODS

Typical manganite $La_{1-x}Sr_xMnO_3$ presents unusual electrical and magnetic properties depending on the doping fraction x.[4] $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) is a metallic ferromagnetic compound at room temperature (Curie temperature $T_C = 370$ K) characterized by small density ($\sim 10^{21}$ cm^{-3}) of highly spin polarized charge carriers.[5]

Our geometry for the standard OLED consists of ITO as hole injector, N,N′-diphenyl-N,N′-(3-methilphenyl)-1, 1′-biphenil-4,4′diamine (TPD) as hole transporting layer (70 nm), 8-hydroxyquinoline aluminum (Alq_3) as emitting layer (70 nm), LiF (2 nm) tunnel barrier, and Al cathode.[1] The manganite work function ϕ_{LSMO} is about 4.7–4.9 eV and is similar to that of ITO ($\phi_{ITO} \sim 5$ eV) allowing the ITO-manganite substitution (Fig. 1).

Epitaxial films of 5-nm-thick LSMO were grown on (100) oriented transparent $SrTiO_3$ substrates by channel-spark ablation[6] using stoichiometric polycrystalline target. The obtained films are metallic and semitransparent with a room temperature resistivity of about 1 mΩ cm.

We compare *IV* and EL curves at ambient conditions of similar OLEDs built up with two different anodes, using as transparent hole injector commercial ITO deposited on glass substrate and LSMO epitaxial film. The emitted light has been collected by a charge coupled device (CCD) camera via an optical fiber placed in front of the transparent substrate. The obtained spectra have been subsequently corrected for instrumental response and for the transmission spectra of ITO–glass and LSMO–$SrTiO_3$, respectively.

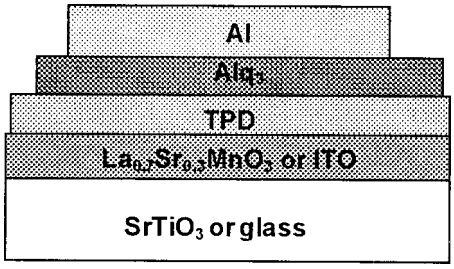

FIG. 1. Schematic view of the OLED devices.

[a)]Author to whom correspondence should be addressed; electronic mail: i.bergenti@ism.bo.cnr.it

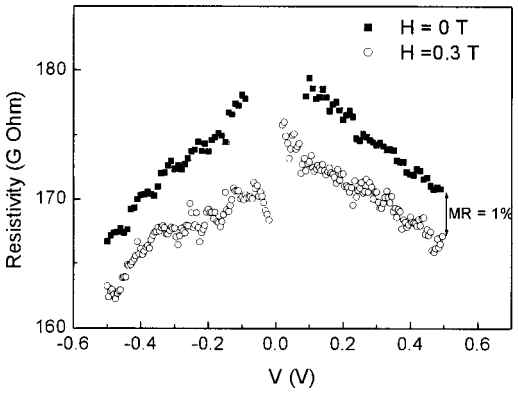

FIG. 2. Resistance curves for TPD in the spin valve geometry (see Ref. 3). Open circles correspond to measurements in an external magnetic field of 0.3 T.

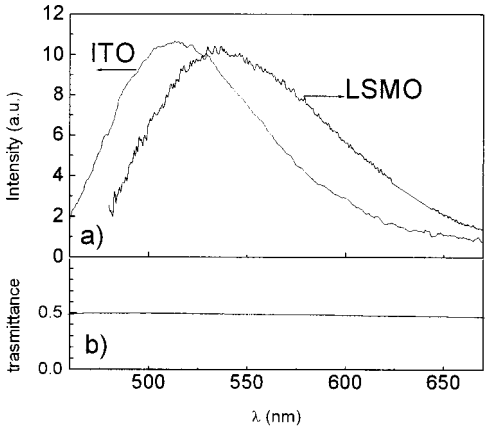

FIG. 4. (a) Electroluminescence spectra for the analyzed two devices corrected for substrate transmission and CCD camera response. (b) Transmittance in the visible range corresponding to manganite thin film deposited on $SrTiO_3$ single crystal.

III. RESULTS AND DISCUSSION

The TPD is acting as hole transport layer between LSMO or ITO and the electroluminescent Alq3. In order to study the spin polarized injection and transport from LSMO into TPD, magnetoresistance measurements have been performed on LSMO–TPD–LSMO spin valve devices with electrodes separated by 100 nm.[3] Applying a static magnetic field of 0.3 T, a magnetoresistance of about 1% at room temperature was observed (see Fig. 2). Despite the limited values, the magnetoresistance effect indicates that, at least partially, the spin polarization is preserved through the organic layer.

The operating characteristics of both LSMO and ITO based OLED (Fig. 3) show typical diode asymmetrical *IV* curves. The threshold voltage and current density for light output vary significantly among the two devices (7 V for LSMO and 3.5 V for ITO) and, for high voltage, the carrier injection in LSMO is significantly higher than in ITO. Detected EL spectrum is very close to the Alq_3 emission band: the spectra of the ITO-OLED have a maximum at nearly 515 nm that is a typical value for Alq3 based OLEDs with different standard cathodes (Al, Mg, Ca...).[2] The LSMO-OLED spectrum is shifted to higher wavelength as shown in Fig. 4(a). This shift cannot be due to the substrate/cathode optical properties. The optical transmission in both cases is almost flat [see, for example, the LSMO transmittance in Fig. 4(b)].

Concerning the light output, ITO is characterized by well uniform emitting surface while in LSMO light is focused on small spots. This behavior can be explained taking into account the presence of large outgrowth structures that are not present on top of the ITO coated glass. At the sharp peaks the effective applied voltage is enhanced and the current as well as exciton density increases. The EL spectrum does not show any linear polarization, as expected for singlet exciton decay.

Under the application of a static magnetic field of about 0.3 T, sufficient to saturate the in-plane magnetization, we do not observe variations in *IV* characteristic or in EL spectrum. The absence of a second spin polarized electrode prevents the observation of any polarization effect. In fact, the external magnetic field induces only the re-orientation of the manganite magnetic domains.

At the moment, the observed shift cannot be correlated directly to the spin polarized injection. In fact, a similar effect has been observed in some OLEDs with nonmagnetic electrodes. By introducing a buffer layer of sexithiophene, between ITO and TPD, a simultaneous increase of current density and a red shift of the EL were observed.[7] Both these effects are also present in our LSMO-OLED. Further investigations are required in order to clarify the origin of the observed EL redshift.

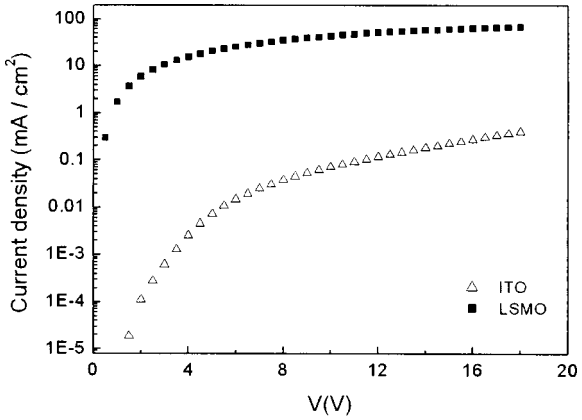

FIG. 3. *IV* curves for ITO (open triangle) and LSMO (full square) based OLED.

ACKNOWLEDGMENT

This work was partially supported by the EC Network Project STEPLED.

[1] J. Kalinowski, J. Phys. D **32**, R179 (1999).
[2] I. H. Campbell and D. L. Smith, *Physics of Organic Electronic Devices* (Academic, New York, 2001).
[3] V. Dediu, M. Murgia, F. C. Matacotta, C. Taliani, and S. Barabanera, Solid State Commun. **122**, 181 (2002).
[4] A. J. Millis, Nature (London) **392**, 147 (1998).
[5] J. H. Park, E. Vescovo, H. J. Kim, C. Kwon, R. Ramesh, and T. Venkatesan, Nature (London) **392**, 794 (1998).
[6] V. Dediu, J. Lopez, F. C. Matacotta, P. Nozar, G. Ruani, R. Zamboni, and C. Taliani, Phys. Status Solidi B **215**, 625 (1999).
[7] D.-M. Shin, S.-T. Lim, J. S. Choi, and J. S. Kim, Thin Solid Films **363**, 268 (2000).